A STATISTICAL STUDY OF THE ALKALI NUMBERS OF VARIOUS STARCHES

by

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INTRODUCTION

The reaction of alkali with starch and starch products has been given considerable study, but at the present time the actual mechanism involved is not clearly understood. In spite of this, the reaction has found many applications both in starch industry and in starch research. The quantity of base consumed is used as the basis for an empirical method for the evaluation of the useful characteristics of starches, and has been found to be correlated with other starch properties such as gel strength, the ratio of cold peak viscosity to that of the hot peak, and the degree of degradation. In industry the measurement of alkali lability (alkali number) is used for quality control; in research it is used for detecting changes in the granular structure.

The alkali number has played an increasingly important part in this laboratory, as a measure of success or failure in attaining certain changes in the starch granule. In order to evaluate such changes, it is necessary to know the precision with which the alkali consumed is measurable for both the natural starch, and the same starch after undergoing experimental treatment.

A survey of alkali number determinations previously made in this laboratory, using a variety of different starches, indicated that the variation of results was not the same for

all starches. A summary of alkali numbers and their deviations are shown in Table 1.

Table 1. The average alkali number and the standard deviation for various starches.

Starch	Sample size	Standard deviation	Average alkali number
Cornstarch SC-1 (Series A)	55	0.33	6.48
Cornstarch SC-1E (Series B)	56	0.27	8.49
Starch Q-1	54	0.14	5.83
Cornstarch No. 7	8	0.18	9.42
Cornstarch N.S.P.	5	0.16	9.49
Extracted Blackhull C-8	5	0.33	9.95

It should be noted that all of these determinations were made by the same operator, presumably under the same conditions. A large number of determinations on the same starch were taken into consideration in some of the above cases, so that the deviation would approach a constant value. However, these deviation values are still very different for the different starches being considered.

In planning a more comprehensive study of the alkali number determination with respect to variability of results when using different starches, it seemed necessary to make certain that the procedure used was uniform for all of the determina-

tions. Previous experience with the alkali number determination had indicated that one possible source of error was that of the titration end point. To avoid inaccuracies due to a color end point fading, (being occluded by the starch suspension) it was decided that a Beckman Model H-2 pH meter should be used for the titration. It was expected that this would not only provide a more exact end point, but also it would enable the operator to follow the complete titration and obtain titration curves for the comparison of different starches.

ALKALI LABILITY

According to practice, starch material may be classified under two headings. First, the part of the granule that is susceptible to alkali breakdown, and second, the part unaffected by alkali treatment. It should be recognized, however, that this classification may not be real in the sense that the parts may be chemically identified within the gross structure of the granule.

Early studies (5) concerning the factors which influence the relative amounts of alkali-labile and alkali-stable portions of the granule were made by T. C. Taylor and his coworkers. Taylor developed the idea that while the initial reducing values of a starch are very small, they may be magnified by treating the starch with hot alkali solution, neutralizing, and then determining the reducing values. He found that only

a portion of the original unaffected starch was stable toward hot alkali. By assuming that the alkali begins its action on the reducing or aldehyde group of the molecule, he explained why the reducing value of the starch was greater after alkali treatment than before.

The alkali labile values are presumed to reflect the properties that are inherent in the particles of starch. These values vary with the plant source and history of the starch. It was found that the more soluble starches had a higher alkali labile value (6). In general, according to prevailing views, the reducing value or the alkali labile value of the starch may increase through either the dissociation of coordinately linked chains, to uncover available aldehyde groups, or by the hydrolytic scission of glucosidic linkages, giving shorter chains and therefore an increased number of aldehyde groups.

The procedure developed by Taylor for the determination of alkali lability values involves the treatment of the starch sample with hot aqueous alkali, the subsequent measurement of the reducing value by treatment with standard iodine solution, and back titration with standard sodium thiosulfate. This procedure is rather difficult to follow accurately, and therefore the results obtained fall short of a satisfactory reproducibility. The time of alkali digestion, the molality of alkali used, time elapsed between titrations, and the pH prevailing during the iodometric titration are all critical

factors. The accuracy depends in large measure on the operator's skill in following precisely the stipulated procedure.

Difficulty with carrying out the Taylor alkali lability determination, and the variable results thereby obtained, led to the simplified Schoch procedure for determining the alkali number. According to Schoch and Jensen (4), the alkali number is the rate of starch-alkali interaction expressed as the number of cubic centimeters of 0.1 N NaOH consumed by one gram of starch during digestion in alkali for one hour at 100° C. The Schoch procedure is an empirical method for determining the index of hydrolytic or other forms of degradation.

If the starch molecule is considered as a glucopyranose chain, terminating in free aldehyde groups, then any glucosidic hydrolysis should be reflected in aldehydic properties. Simple acidic and aldehydic products, including formic, acetic and lactic acids, and pyruvic aldehyde, have been isolated from alkali treated starches in aqueous solutions.

It was found that Schoch's alkali number varied according to the pre-treatment of the starch, in a manner similar to that of the alkali-labile value of Taylor. Cornstarch treated with hot alkali, neutralized, and precipitated with alcohol, was found to have a lower alkali number than the original starch. However, when such a digestion is continued until 80 to 90 per cent of the starch is destroyed, the alkali number of the residual starch does not drop below 4.0, indicating that no fraction of the original starch is entirely stable toward

alkali (4). More recent experiments have shown that starches with an alkali number as low as 0.4 may be prepared, in contradiction to the previous theory.

The exact cause for variance in the alkali number has not yet been accurately determined. It is known that various pretreatments of the starch cause a consistent change in the alkali number value. Some physical properties, particularly the hot and cold peaks of viscosity measurements are known to be closely related to the alkali number. The value of the alkali number seems to be a function of several factors, rather than any single one. Usually (although not always), the breakdown of the starch granule into smaller units by either physical or chemical means serves to increase the value of the alkali number.

METHOD OF STATISTICAL TREATMENT OF ALKALI NUMBER VALUES

When a population of numerical measurements involves so much data that it is impossible to analyze the whole of it, sampling must be relied upon to furnish the desired information. In the case of analytical determinations, such as the alkali number of starch, the procedure may be repeated a number of times, but the values obtained will be at least slightly different each time. In order to evaluate data obtained from such a sample, and to show the relationship between it and the

true values, statistical methods must be applied.

It is assumed that the experimental data form a normal frequency distribution curve. Such a curve would be symmetrical, with the average value of all determinations having the greatest frequency of occurrence. The distribution of alkali number values for a single starch may be shown to approximate such a curve.

The normal distribution curve may be defined in terms of the standard deviation, σ, and the mean, m. The mean is the arithmetical average and may be expressed as:

$$m = \frac{\sum x_1}{n}$$

The standard deviation is a measure of the dispersion of data about the mean. It may be expressed as:

$$\sigma = \sqrt{\frac{(x_1 - m)^2}{n}} \qquad = \sqrt{\frac{\sum x_1^2 - \frac{(\sum x_1)^2}{n}}{n}}$$

where x_1 represents the datum for a single chemical analysis, and n is the number of such data in the population.

Each sample drawn from a normal distribution will nearly always be different from every other sample taken from the same population; yet certain features of these samples, as a group, will tend to conform to a predicable pattern.

When the values for m and σ for a normal population are unknown, as is the case with any analytical data, they are best estimated by the following equations (2):

$$\bar{x} = \frac{\sum x_i}{k}$$

k = number of data in the sample

$\bar{x}$ = sample mean

x_i = individual datum

and

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{k-1}}$$

It should be noted that the calculation of s is similar to that of σ, except for two differences:

1) $\bar{x}$ replaces the mean, m.
2) the divisor is k-1 instead of n.

If, in a normal population, the difference between individual datum and the population mean is expressed as a ratio to σ, $\frac{x_i - m}{\sigma}$, the resulting function is also normally distributed. However, when the standard deviation is unknown, as is usually the case, the corresponding ratio expressed as the function of t_i,

$$t_i = \frac{\bar{x}_i - m}{s_{\bar{x}}} \qquad \text{where } s_{\bar{x}} = s/\sqrt{k}$$

is not normally distributed. The distribution of t_i depends upon the sample size as well as the variable x_i.

When the true population mean, m, is not known, it is still possible to fix its value within certain limits and with a certain probability. An inequality for "t" may be rewritten in the following form:

$$-t_1 \left\langle \frac{\bar{x}_1 - m}{s_{\bar{x}}} \right\langle t_1$$

or

$$\bar{x}_1 - t_1 \, s_{\bar{x}} \left\langle m \right\langle \bar{x}_1 + t_1 \, s_{\bar{x}}$$

The values of $\bar{x}_1$ and $s_{\bar{x}}$ are obtained from sample data, and the values for t_1, corresponding to the sample size and the desired probability level, may be obtained from statistical tables (2).

METHOD OF COMPARISON OF INITIAL POINTS ON TITRATION CURVES

In comparing the initial pH of the alkaline starch suspension with that of a blank determination, it is necessary to determine if any difference between the two values is significant. In this case, there are a large number of initial pH values for a single starch, with which to compare an equally large number of pH values for the corresponding blank determinations.

The following equations are given as a means of determining statistically if there is a significant difference between these two populations (2).

$$s_{\bar{d}} = \sqrt{\frac{\sum x_1^2 + \sum x_2^2}{k(k-1)}}$$

where:

$s_{\bar{d}}$ = the standard deviation of sample difference

x_1 = the difference between individual datum and the arithmetical mean of sample 1.

x_2 = the difference between individual datum and the arithmetical mean of sample 2.

k = the number of individual data in either sample 1 or 2.

$\bar{d} = \bar{x}_1 - \bar{x}_2$ where: $\bar{x}_1$ = arithmetical average of sample 1.

$\bar{x}_2$ = arithmetical average of sample 2.

It can be shown that the ratio, $\bar{d} / s_{\bar{d}}$, follows the same "t" distribution as mentioned in the previous section. By use of the "t" distribution table, the corresponding probability that the two populations are identical can be obtained.

APPARATUS

An apparatus generally suitable for making electrometric titrations was suggested by Louis B. Rockland and Max S. Dunn (3). By making a few changes in the apparatus described by these authors, it was readily adapted to the alkali number determination.

The titration cup was a pyrex funnel with a six mm stopcock sealed on the funnel stem. The outlet of the cup was a rubber tube, which could be connected to a water aspirator.

A 50 ml burette, with a curved tip, was held by a burette clamp in such a manner that it was directly over the center of the titration cup. It could be removed easily for refilling from a five gallon bottle of standard acid.

A cone drive electric stirrer was clamped to the ring stand and the stirring rod was fastened directly to the chuck

of the stirrer by means of a small length of rubber tubing. The bearing for the stirring rod was made from a standard ground glass ball-socket type joint, the top part of which was fastened to the stirring rod by means of a small one-hole cork, and the bottom half of the joint was clamped firmly to the ring stand.

The pH meter electrodes were held by an electrode clamp, which was fastened to a 6-inch length of 1/8-inch steel rod that was clamped to the ring stand. The electrodes were connected to the pH meter by means of 30-inch leads. The principal parts of the apparatus are shown in Plate I.

EXPLANATION OF PLATE I

A - Titration cup

B - pH meter electrodes

C - Glass stirring rod

D - Stirring rod bearing

E - Ring stand base

F - Electrode wires leading to pH meter

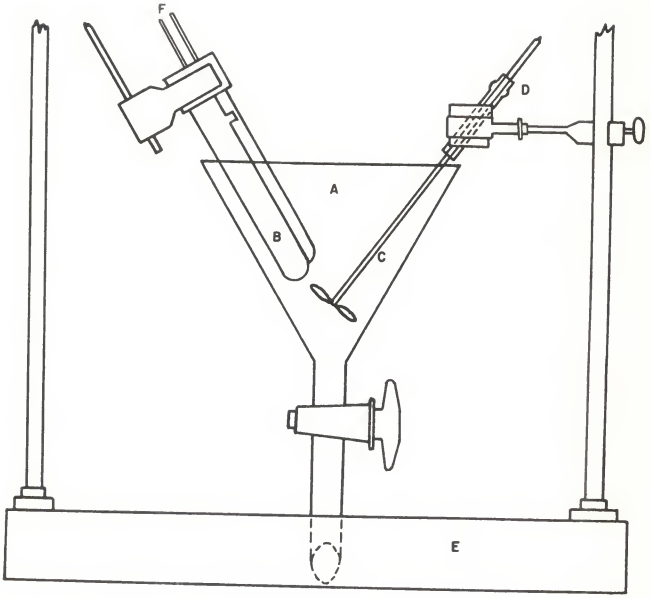

PLATE I

PROCEDURE

The Schoch method for determining alkali numbers has been modified in some respects, particularly in regard to the method of the final titration. The procedure used in this work may be described as follows:

1. A 500 mg sample (dry basis) of a starch was introduced into an 8 oz. Pyrex nursing bottle.

2. 20 cc of boiled distilled water was added and the contents swirled to give a uniform suspension.

3. Exactly 25 ml of 0.4 N NaOH was added by means of a burette, with constant agitation to insure uniform gelatinization. If lumping occurred at this point the sample was discarded and the above procedure repeated.

4. 55 cc of near-boiling distilled water was added and the bottle capped with a 1-hole rubber stopper. The bottle then was placed in a boiling water bath.

5. The sample was heated for exactly one hour, then removed and placed in a cold water bath. The cap was removed and 65 cc of cold distilled water added.

6. The stop-cock attached to the funnel was closed and the contents of the nursing bottle carefully transferred to the titration cup. The bottle was rinsed three times with 15 cc portions of distilled water. The stirrer and pH meter were put into operation, care being taken to see that the tips of the electrodes were well beneath the surface of the liquid.

7. The sample was titrated with 0.2 N H_2SO_4 to an end point pH of 7.00.

8. After the titration was completed, the stirrer was shut off, the pH meter changed to the neutral position, and the contents of the titration cup drained by opening the stopcock. The apparatus was then ready for the next sample.

A blank determination was run using the same procedure, but without the starch. The alkali number then is calculated by means of the Schoch equation (4):

$$\text{Alkali No.} = \frac{\text{Normality of acid (Vol}_{\text{blank}} - \text{Vol}_{\text{sample}}) \times 10}{\text{Weight of sample in grams}}$$

The starches used in this work were selected to include those giving both high and low alkali number values. Thus it became possible to compare the reliability of the alkali numbers through the range of starches from glutinous to non-glutinous varieties. The data necessary for titration curves were taken at the same time as that for the alkali number determinations.

EXPERIMENTAL RESULTS

Alkali Numbers of Various Starches

The starches used in this work, with their corresponding average alkali numbers and limits of reliability are shown in

Table 2. The limits of reliability, as calculated for these starches, are for a probability level of 0.99.

Table 2. Average alkali numbers for various starches using the electrometric titration procedure.

Starch	Sample size	Standard deviation	Average alkali no.	Limits
Natural Pink Kafir	53	0.38	6.25	±0.14
Extracted Pink Kafir	51	0.38	8.34	±0.14
Cornstarch SC-1 (Series A)	20	0.33	6.68	±0.22
Cornstarch SC-1E (Series B)	20	0.20	8.45	±0.13
Starch 190 (Double Dwarf Waxy Milo)	25	0.40	2.75	±0.22
Starch 190-E (Extracted)	25	0.33	3.32	±0.19
Maine Potato Starch	10	0.46	4.17	±0.46
Maine Potato Starch (Extracted)	10	0.35	3.51	±0.37
Tapioca Starch, N.S.P.	5	0.13	5.39	±0.25
Tapioca Starch, N.S.P. (Extracted)	5	0.17	5.42	±0.33

Average Data for Titration Curves

The data necessary for titration curves were recorded at the same time the alkali numbers of Table 2 were determined. The averages of these data, with those of their corresponding alkali numbers, are shown in Table 3.

Titration curves for extracted Pink Kafir and Double Dwarf Waxy Milo starches are shown in Figs. 1 and 2. These curves utilize data from Table 3, and can be considered as typical of the curves which could be obtained for the other starches listed in Table 3.

Table 3. Average data for the titration curves for various starches and their corresponding blanks.

Vol. of acid added:	Native starch pH	Native starch Sample size	Blank pH	Blank Sample size	Extr. starch pH	Extr. starch Sample size	Blank pH	Blank Sample size
				Pink kafir starch				
0.0	11.91	53	11.90	22	11.90	51	11.90	22
35.0	11.52	40	11.53	22	11.50	41	11.53	22
40.0	11.32	43	11.37	22	11.26	41	11.37	22
43.0	11.07	43	11.18	22	10.94	41	11.18	22
45.0	10.70	43	10.95	22	10.32	41	10.95	22
46.0	10.22	43	10.75	22	9.65	41	10.75	22
47.0	9.44	43	10.37	22	8.11	34	10.37	22
48.0			9.74	22			9.74	22
End Pt.	47.80	53	49.34	22	47.29	51	49.34	22
				Cornstarch SC-1				
0.0	11.89	16	11.89	8	11.88	16	11.89	8
35.0	11.49	10	11.54	3	11.48	10	11.54	3
40.0	11.29	10	11.41	4	11.26	10	11.41	4
43.0	11.06	10	11.23	4	11.00	10	11.23	4
45.0	10.77	10	11.05	4	10.64	10	11.05	4
46.0	10.47	10	10.89	4	10.20	10	10.89	4
47.0	9.91	10	10.66	4	9.43	10	10.66	4
48.0	8.40	9	10.21	4			10.21	4
End Pt.	48.02	20	49.66	8	47.58	20	49.66	8

Table 3. (concl.)

Vol. of acid added	Native starch pH	Native starch Sample size	Blank pH	Blank Sample size	Extr. starch pH	Extr. starch Sample size	Blank pH	Blank Sample size
			Starch 190, Double Dwarf waxy milo					
0.0	11.67	7	11.72	5	11.71	11	11.72	5
35.0	11.20	3	11.40	1	11.16	4	11.40	1
40.0	11.03	3	11.20	1	10.95	4	11.20	1
43.0	10.79	3	11.04	1	10.76	4	11.04	1
45.0	10.51	3	10.84	1	10.53	4	10.84	1
46.0	10.31	3	10.68	1	10.32	4	10.68	1
47.0	9.94	3	10.45	1	9.95	4	10.45	1
48.0	9.21	3	10.00	1	9.30	4	10.00	1
End Pt.	49.21	25	49.91	5	48.91	25	49.91	5
			Maine potato starch					
0.0	11.76	8	11.80	1	11.70	1	11.80	1
35.0	11.31	4	11.38	1	11.30	1	11.38	1
40.0	11.12	4	11.18	1	11.11	1	11.18	1
43.0	10.88	4	11.02	1	10.85	1	11.02	1
45.0	10.58	4	10.82	1	10.60	1	10.82	1
46.0	10.33	4	10.68	1	10.30	1	10.68	1
47.0	9.80	4	9.91	1	9.86	1	9.91	1
48.0	8.80	3	8.40	1	9.09	1	8.40	1
End Pt.	48.63	10	49.70	2	48.79	10	49.70	2

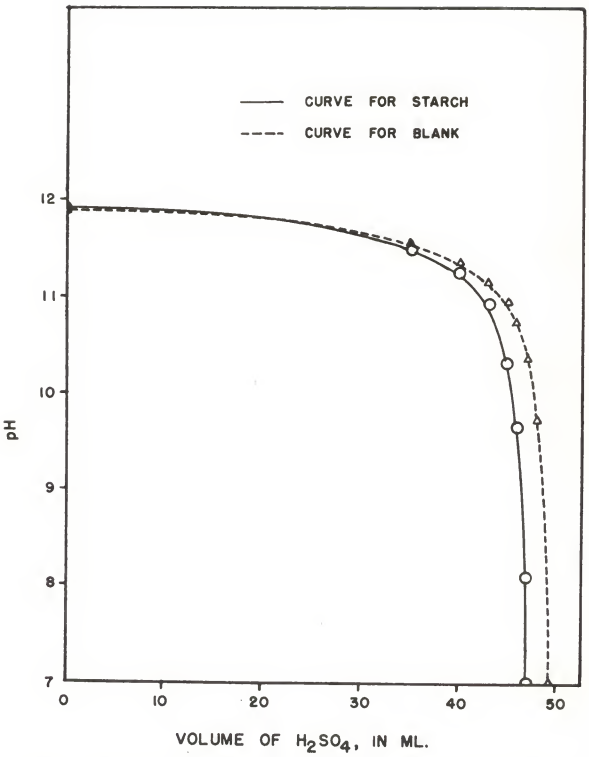

Fig. 1. Electrometric titration curve for extracted Pink Kafir starch.

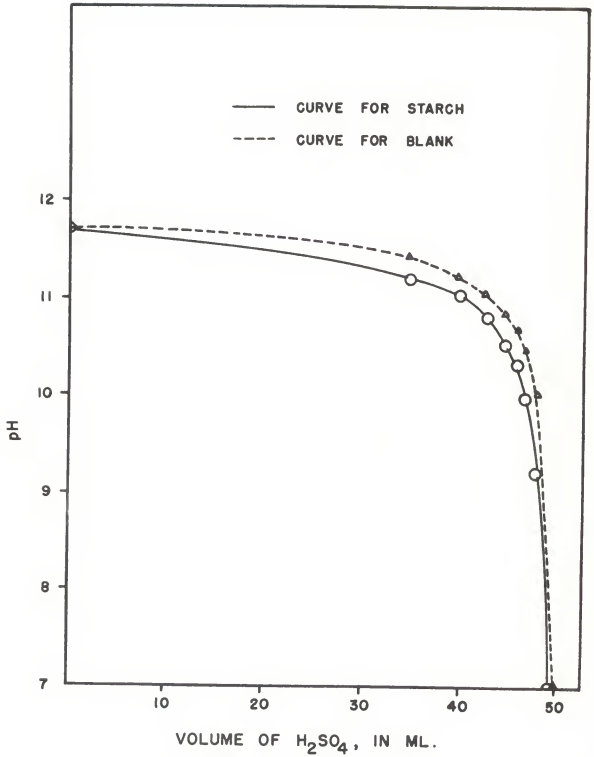

Fig. 2. Electrometric titration curve for Double Dwarf Waxy Milo starch.

Comparison of Initial Points on Titration Curves

The average initial pH values for the final titration in the alkali number determination are shown in Table 4. The pH values for the various starches are compared with the corresponding values for the blank determinations. The probability that any difference between these values is a real difference and not just due to variation in results is also shown.

Table 4. Comparison of initial points on titration curves with those of the corresponding blank.

Starch	Sample size	Initial pH for starch	Initial pH for blank	Difference	Prob. diff. is real
Pink kafir	53	11.91	11.90	+0.01	approx. .50
Pink kafir extr.	51	11.90	11.90	0.00	0
Cornstarch SC-1 (Series A)	16	11.89	11.89	0.00	0
Cornstarch SC-1E (Series B)	16	11.88	11.89	-0.01	.67
Starch 190 (Double dwarf waxy milo)	7	11.67	11.72	-0.05	.74
Starch 190-E extracted	11	11.71	11.72	-0.01	.15
Maine potato starch	8	11.76	11.80	-0.04	insuf. data
Maine potato starch extr.	1	11.70	11.80	-0.10	
Tapioca starch	5	11.84	11.80	+0.04	
Tapioca starch extracted	3	11.88	11.80	+0.08	

DISCUSSION AND CONCLUSION

The accuracy of the electrometric titration method of determining the alkali number for starches is approximately the same as that for the regular Schoch procedure which employs a colorimetric end point. The standard deviations for the same starch using the two different procedures are compared in Table 5.

Table 5. Comparison of standard deviations using the color and electrometric end points.

Starch	Color end point		Electrometric end point	
	Sample size	Standard deviation	Sample size	Standard deviation
SC-1 (Series A)	55	0.33	20	0.33
SC-1E (Series B)	56	0.27	20	0.20

Even though the electrometric titration is not more accurate than that in which a color end point is used, its use would be advantageous for the titration of highly colored or turbid solutions. Both methods require for completion about the same length of time.

The titration curve shown in Fig. 1, representing the determination of alkali number for extracted Pink kafir starch, is typical of that obtained in a normal acid-base titration. The

curve for the starch titration follows the same general contour as that for the blank titration.

When comparing the initial pH values of the starches with the corresponding values for the blanks (Table 4) in no case can the difference in pH be considered as being a real difference. However, in some cases the probability of this difference being real is greater than the probability that the difference is not real. If the starches shown in Table 4 are classified as to being either glutinous or non-glutinous varieties, there appears to be a trend that the non-glutinous starches have little or no difference in pH between the starch and the blank determinations, while the titrations of glutinous starches consistently show lower initial pH values than do those for the corresponding blank determinations. This is shown more clearly in Table 6.

Table 6. Classification of starches and the corresponding difference in initial pH values between the starch and the blank.

Glutinous varieties		Non-glutinous varieties	
Starch	Diff. in pH	Starch	Diff. in pH
Starch 190	-0.05	Pink kafir	+0.01
Starch 190 extracted	-0.01	Pink kafir extracted	0.00
Maine potato starch	-0.04	Cornstarch SC-1	0.00
Maine potato starch extracted	-0.10	Cornstarch SC-1E extracted	-0.01

Apparently while the glutinous type starches are going through the "cooking" period in the alkali number determination, part of the alkali becomes entrapped in the highly branched structure of the starch granule, and remains entrapped until neutralization is nearly completed during titration with standard acid. The non-glutinous varieties are generally thought to have a more stereotyped structure, more regularity in the branching of the molecule, and less branching than the glutinous varieties. If this is true, then one could expect to obtain more consistent and more precise chemical reactions with the non-glutinous types of starch than with the glutinous types.

The standard deviation of the alkali numbers, as shown in Table 2, may be considered as a measure of the uniformity of the reaction between alkali and starch. The smaller the standard deviation, the more consistent are the initial points of contact and following reaction between alkali and starch. As the standard deviation decreases, the probability that the chemical reaction will follow a given path increases.

In all of the cases in Table 2, except for the Tapioca starches, the extracted starches have a lower standard deviation than the original natural starches, and yet have a higher value for the alkali number. This can be explained on the basis of a more formalized structure in the extracted starches than in the natural starches. Most pre-treatments of starch, including solvent extraction, are thought to produce a more

highly uniform structure in the starch granule. The extracted starches are more completely degraded in the alkali number determination than are the natural starches, as indicated by the alkali number values, but they are degraded in a more consistent manner.

If the primary focal points of reaction with alkali were the terminal aldehyde groups of the starch substance, as is generally believed, then a lower standard deviation would indicate a lower, rather than a higher, alkali consumption. This may be so interpreted on the basis that a change toward a greater definition of structure, as is indicated by a greater probability of a definite reaction pattern, would tend to restrict by screening the availability of alkali-labile functional groups. Thus, the present work supports previously obtained findings of this laboratory that the capacity of a starch to consume alkali does not depend primarily on the incidence of aldehyde groups (1). Rather is it probable that the alkali-labile structures, not functional groups in the usual sense, are formed for the most part during the gelatinization process which occurs as a part of the alkali number determination.

While the use of statistical methods is probably too time consuming for many routine determinations, it does provide a method for learning the precision of certain analytical data. In the study of large molecules, many of the usual methods of determining structure are inadequate due to the variability and complexity in physical structure and, in many cases, the

dependence of chemical reactions upon gross physical structure. The use of statistical methods may provide an insight into some of the causes of variation in analytical results from the standpoint of molecular structure.

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1951

Although the reaction between alkali and starch has been given considerable study, the actual mechanism of the reaction has not yet been clearly explained. However, the concept most generally held is that the alkali consumed by a starch is a measure of its terminal aldelyde groups.

One of the most widely used measurements of the extent of reaction between alkali and starch is that of the alkali number. According to T. J. Schoch, the alkali number is the rate of decomposition of starch, expressed as the number of cubic centimeters of 0.1 N NaOH consumed by one gram of starch during digestion in alkali for one hour at 100° C.

A survey of alkali number determinations previously made in this laboratory indicated that the variation of alkali number values was not the same for all starches. The purpose of this work was to study further the variation of alkali numbers with respect to starch structure. In order to obtain the most consistent results possible, the Schoch procedure for determining the alkali numbers was modified to include an electrometric titration rather than one with a color end point. Data for titration curves were obtained at the same time the alkali numbers were determined.

A sufficiently large number of alkali number determinations was obtained on each of several starches used, so that a comparison of the standard deviations would be possible.

A series of alkali number determinations for the same starch was made, using both the original Schoch procedure and the modified procedure with the electrometric titration. The results indicated that the precision of the two procedures was virtually identical.

When the standard deviations of the alkali numbers for various natural starches were compared with the same starches after solvent extraction, it was noted that the standard deviations of the extracted starches were consistently lower than those of the corresponding original starches. The lowered standard deviation, in the case of the extracted starches, indicates that the reaction between alkali and starch is approaching a more nearly uniform pattern. This, together with other work in this laboratory, provides evidence that the reaction between alkali and starch cannot be satisfactorily explained on the basis of terminal aldehyde groups alone. If the alkali number depends upon the lattice structure of the starch granule, rather than upon functional groups (terminal aldehyde groups) initially present in the granule, then the decreased standard deviation may be interpreted as showing an increase in the formalized structure of the granule.